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Morphological study of aluminum *tris*(8-hydroxyquinoline) thin films using infrared and Raman spectroscopy

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We present comprehensive Raman spectra for thin films of Alq₃, annealed at various temperatures up to 300 °C, over the range of 70–1800 cm⁻¹. These spectra give strong evidence for structural rearrangement of thin films of Alq₃ upon annealing at temperatures above 200 °C. Needle like crystals are observed to grow in the films and confirmed to be comprised of the α -Alq₃ polymorph using the low energy Raman spectra. Furthermore, no evidence of the *fac* isomer or thermal interconversion between the *mer* and *fac* isomers of Alq₃ was observed in either the infrared or Raman spectra of the thin films or powder. These results may have implications for the long-term efficiencies of organic light emitting diodes incorporating thin films of Alq₃. © 2002 American Institute of Physics. [DOI: 10.1063/1.1495527]

INTRODUCTION

Aluminum *tris*(8-hydroxyquinoline) (Alq₃) is one of the most widely used molecules in organic light emitting diodes (OLEDs) following the demonstration of an efficient device utilizing the molecule.¹ In addition to earlier studies of Alq₃,^{2–6} this use of the molecule for OLED applications has lead to a number of more recent studies.^{7–20} Despite all this research the role of the morphology of Alq₃ films on the performance and stability of OLEDs incorporating them is still not clear.

Two geometric isomers of Alq₃ exist, *mer* (C₁ symmetry) and *fac* (C₃ symmetry), and thermal interconversion between the two has previously been suggested.⁵ Evidence suggests that such interconversion is not a prerequisite for obtaining amorphous films.¹⁶ However, it has been suggested that the two isomers coexist in the amorphous state, which may result in an increase in the stability of this state.¹⁸ Additionally it is thought that the *fac* isomer, even as a minority isomer, may play an important role in devices as it is a more efficient electron trap than the *mer* isomer.¹⁴ Studies using density functional calculations and Hartree–Fock analysis of the isomers indicate that they can be identified using Raman and infrared (IR) spectroscopy^{13,17,20} although to date no spectral evidence of the *fac* isomer has been reported.

Detailed studies of the *mer* isomer have revealed that three different polymorphs of Alq₃ can exist, labeled α -Alq₃, β -Alq₃, and γ -Alq₃.¹⁶ The first two of these polymorphs were identified using Raman spectroscopy.

To date the majority of IR spectra that have been reported were obtained from Alq₃ powder dispersed in KBr^{13,16,20} or an argon matrix.¹⁷ One reflection–absorption

IR spectra has been published of a 200 nm film although no data below 700 cm⁻¹ was presented.¹³ Published Raman spectra are all obtained from Alq₃ in the solid state.^{13,16,20}

In this work we give detailed IR and Raman spectra of Alq₃ powder and thin films annealed at temperatures ranging from ambient to 300 °C. The Raman spectra obtained cover the range 70–1800 cm⁻¹ thus enabling the morphology of thin films to be studied and compared to previous work on solid Alq₃. IR spectra of the thin films were also obtained from 270 to 2000 cm⁻¹, although only the previously unpublished region below 670 cm⁻¹ for thin films is presented. We then discuss the results and their implications for OLEDs based on thin layers of Alq₃.

EXPERIMENTAL METHOD

The Alq₃ powder was obtained from Aldrich and used without further purification. Films of Alq₃ were sublimed under a vacuum of $\sim 10^{-6}$ mbar at a rate of 1–2 Å/s onto WSi₂ and KBr substrates. The substrate temperature was not controlled and the resulting Alq₃ film thicknesses were 635 nm on the WSi₂ and 50 nm on the KBr substrates, measured using a calibrated quartz crystal thickness monitor.

Annealing of the films was carried out under a flowing nitrogen atmosphere using a barrel furnace. Each anneal was for 1 h at a temperature of 50, 100, 150, 200, 225, 250, or 300 °C.

KBr disks incorporating Alq₃ powder (0.1% by weight) were also prepared. The IR absorption spectra were obtained using a Perkin Elmer 2000 Fourier transform IR spectrometer with a resolution of 0.5 cm⁻¹. The Stokes Raman spectra were obtained using a Renishaw Raman microscope with an excitation wavelength of 244 nm. The anti-Stokes Raman spectra (-500 to -70 cm⁻¹), observed due to photoluminescence obscuring the Stokes lines, were obtained using a Ren-

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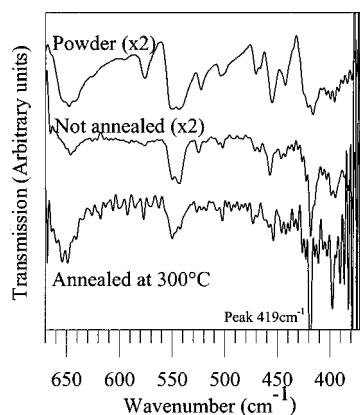


FIG. 1. The IR transmission spectra of Alq_3 powder dispersed in a KBr disk, a 50 nm sublimed film of Alq_3 , and a 50 nm sublimed film of Alq_3 following annealing at 300 °C.

ishaw Raman microscope system fitted with a Leica DMCN microscope incorporating a charge coupled device (CCD) camera. The excitation source used was a 632 nm HeNe laser and the system had a resolution of better than 1 cm^{-1} . The images of the Alq_3 sublimed films were obtained using the CCD camera on the microscope using a $\times 20$ objective. All Raman spectra were taken using a $\times 50$ objective.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectra of Alq_3 powder dispersed in a KBr disk and two sublimed films of Alq_3 (on KBr substrates) one of which has been annealed at 300 °C. Similarly, Fig. 2 shows the Raman spectra for Alq_3 powder and sublimed films on WSi_2 substrates obtained using the 244 nm excitation source. The IR spectrum of the powder clearly shows what appears to be two sets of doublet peaks at ~ 550 and $\sim 650 \text{ cm}^{-1}$ and a single peak at 523 cm^{-1} that correspond to the Al–O stretching modes of the *mer* isomer of Alq_3 .^{17,20} Figure 2 shows a similar set of doublets centered at ~ 540 and 640 cm^{-1} . Simulated Raman and IR spectra both indicate that the *fac* isomer exhibits only a single peak at these positions.^{13,17} Therefore the observation of doublets at these positions is strong evidence that the *mer* isomer is the predominant species in both the powder and the sublimed film reported here. The annealing at 300 °C of the Alq_3 film has little effect on the position of these peaks in the IR and Raman spectra but does appear to increase the resolution of the doublet structures. Interestingly the peaks centered at $\sim 550 \text{ cm}^{-1}$ in the IR spectrum appear to be comprised of at least three peaks centered at 542, 548, and 550 cm^{-1} . The emergence of a third peak is not evidence of any thermal interconversion between the *mer* and *fac* isomer but may be the result of a change in the packing of the Alq_3 following annealing as will be discussed later.

The other noticeable effect of annealing is to significantly increase the strength of the IR absorption peaks observed at 418 and 398 cm^{-1} , thus helping to resolve the multiplets centered on these peaks. These absorptions have been associated with O–Al stretching and C–O–Al bending

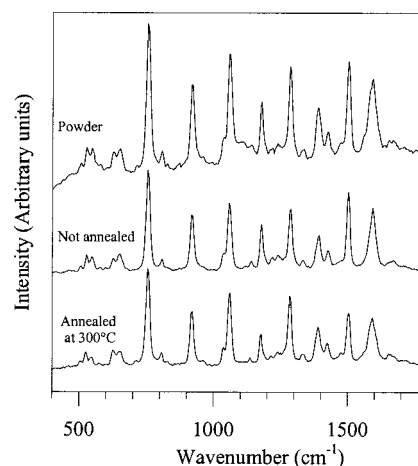


FIG. 2. The Raman spectra of Alq_3 powder, a 635 nm sublimed film of Alq_3 , and a 635 nm sublimed film of Alq_3 following annealing at 300 °C.

modes. It might be expected that an increase in the packing order would have the effect of enhancing some of these modes while reducing others.

Brinkmann *et al.* showed that there exists at least three phases of *mer* Alq_3 and showed that the α and β phase could be distinguished using low energy Raman spectra.¹⁶ Figure 3 shows such a Raman spectra of Alq_3 powder, a sublimed film of Alq_3 (on a WSi_2 substrate), and various areas of sublimed films annealed at 225 and 300 °C over the range -500 to -70 cm^{-1} . Figure 4 shows microscope images of the regions of the sublimed films that the spectra shown in Fig. 3 were obtained. The Raman spectrum of the Alq_3 powder shows a main broad peak centered at 109 cm^{-1} with a shoulder at $\sim 95 \text{ cm}^{-1}$. Within this broad peak lie two of the Raman “fingerprints” used to identify the α - Alq_3 and β - Alq_3 , at 117 and 109 cm^{-1} , respectively.¹⁶ The origin of this broad peak is still somewhat unclear. Calculations of the vibrational modes for both the *mer* and *fac* isomers do not predict any modes between ~ 135 and 55 cm^{-1} .^{13,17,20} However, the frequency of such low energy modes is highly dependent on the molecular arrangement (hence the ability to distinguish between the two polymorphs). Currently it is thought that this broad peak originates from vibrations of the central Al ion mainly involving the torsional O–Al and N–Al modes.²⁰

In addition to the main peak two other peaks are visible at 155 and 165 cm^{-1} . The former of these peaks coincides with the second Raman fingerprint of α - Alq_3 and both result from modes involving the O–Al–N bonds, the “butterfly” modes of the ligands.^{17,20} The position of the main peak, the peak at 152 cm^{-1} , along with the lack of any peak at 183 cm^{-1} suggests that the powder is comprised of mainly the α - Alq_3 polymorph.

If we compare the Raman spectra of the Alq_3 powder and sublimed film that has not been annealed, shown in Fig. 4(a), there are some obvious differences. First the main broad peak has moved from 108 to 95 cm^{-1} upon sublimation of the Alq_3 . Additionally the peak at 152 cm^{-1} has reduced in intensity while a peak at 194 cm^{-1} , related to a torsional N–Al mode, has emerged. Also apparent is a broad-

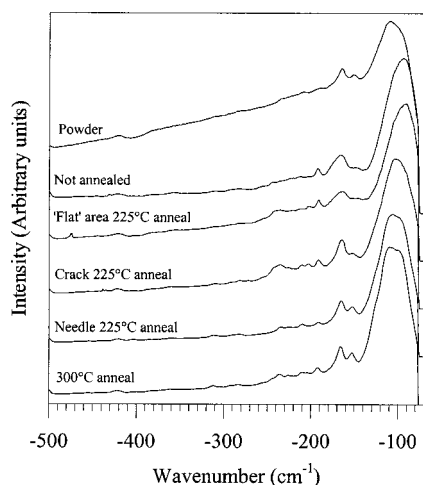


FIG. 3. The 632 nm excited Raman spectra of Alq_3 powder, a 635 nm Alq_3 film as deposited, three areas of a 635 nm Alq_3 film annealed at 225 °C for 1 h, and a 635 nm Alq_3 film annealed at 300 °C for 1 h.

ening of the peak at 165 cm^{-1} with close inspection revealing a peak centered at $\sim 176\text{ cm}^{-1}$. The reduction in the presence of the $\alpha\text{-Alq}_3$ fingerprints along with no evidence of the $\beta\text{-Alq}_3$ polymorph is consistent with the deposited film being amorphous. There is a possibility that the sublimed film may be comprised of the disordered $\gamma\text{-Alq}_3$ polymorph. However, given that the $\alpha\text{-Alq}_3$ to $\gamma\text{-Alq}_3$ conversion occurs above 395 °C,¹⁷ which is above the sublimation temperature used, we feel that this is unlikely. As has been previously noted for the reflection-absorption IR spectra of 200 nm Alq_3 films¹³ we observed no change in the IR or Raman spectra upon annealing of the sublimed films at temperatures up to 200 °C. At temperatures above this, however, the films are seen to start crystallizing as expected from thermal analysis of Alq_3 .⁹ The Raman spectra of three areas of a film annealed at 225 °C, Fig. 4(b), are shown in Fig. 3. The Raman spectrum of the featureless area of the film, labeled “flat” area, is similar to that of the unannealed film. However, changes can be seen in the spectra obtained from a crack in the film and a small needle like crystal (similar to that described by Brinkmann *et al.*¹⁶). In both of these spectra the main peak has moved back from 95 cm^{-1} toward the position observed in the spectrum obtained from the Alq_3 powder. Furthermore, the peak at 152 cm^{-1} has re-emerged. Finally, Fig. 3 shows the Raman spectrum of the film annealed at 300 °C, shown in Fig. 4(d). This film is almost entirely comprised of many needle like crystals. The Raman spectrum shows the characteristic $\alpha\text{-Alq}_3$ fingerprint at 154 cm^{-1} and a shoulder in the main peak at $\sim 120\text{ cm}^{-1}$ indicates the presence of the second fingerprint of this polymorph. The main peak can be seen to consist of two further peaks centered at 109 and 100 cm^{-1} . The peak at 109 cm^{-1} may suggest that there is some of the $\beta\text{-Alq}_3$ polymorph present although no corresponding peak is observed at 183 cm^{-1} . Additionally, peaks can be seen in the high-energy tail at $\sim 422, 311, 283,$ and 235 cm^{-1} as previously described for Alq_3 .²⁰

No Raman signals could be obtained for the 50 nm thick films on KBr substrates in the region below 400 cm^{-1} . How-

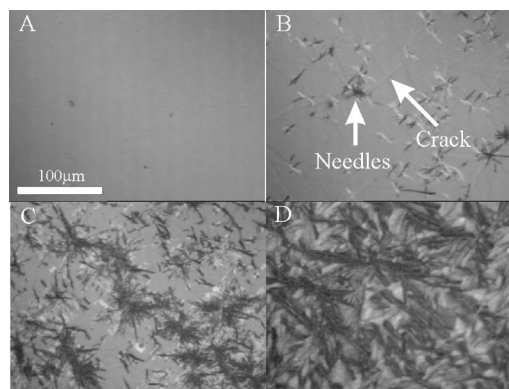


FIG. 4. Optical microscope images of: (a) an as deposited 635 nm Alq_3 film, (b) a 635 nm Alq_3 film annealed at 225 °C for 1 h, (c) a 635 nm Alq_3 film annealed at 250 °C for 1 h, and (d) a 635 nm Alq_3 film annealed at 300 °C for 1 h. Each image was taken using a $\times 20$ objective.

ever, the surface of the films did appear to change when viewed under a microscope after annealing at 300 °C. This along with the changes observed for the thicker 635 nm films upon annealing suggest that some structural rearrangement has occurred in these films. Such an effect could explain the subtle changes observed in the IR spectra in Fig. 1. The possibility that these changes are due to volatile impurities incorporated into the films during sublimation being driven off cannot be ruled out. However, although the Alq_3 was used as received, earlier “sacrificial” sublimations prior to the deposition of the films reported here would have significantly reduced this risk.

The results presented here have implications for OLED devices incorporating Alq_3 . No evidence of the *fac* isomer or thermal interconversion between the *mer* and *fac* isomers was found. The inability to observe the *fac* isomer makes any future analysis of the importance of the isomer in trapping electrons difficult. Indeed the isomer may not be present even as a minority within the films.

The change in morphology with annealing may have implications for devices with long operational lifetimes. Such a rearrangement of the film over a long time span may introduce nonradiative trap sites that will reduce the device efficiency. This rearrangement would tend to proceed quicker in device “hot spots” (e.g., areas of high current density), which then could act as “seeds” for more structural change thus reducing the efficiency further.

CONCLUSIONS

In conclusion we have presented comprehensive Raman spectra for thin films of Alq_3 annealed at various temperatures between ambient and 300 °C. These spectra give strong evidence for a structural rearrangement of the molecular packing within thin films of Alq_3 upon annealing at temperatures above 200 °C. Needle like crystals are observed to grow in the films and confirmed to be comprised of the $\alpha\text{-Alq}_3$ polymorph using the low energy Raman spectra. Furthermore, no evidence of the *fac* isomer or thermal interconversion between the *mer* and *fac* isomers was observed in

either the IR or Raman spectra of the thin films or powder. These results may have implications for the long-term efficiencies of OLEDs incorporating thin films of Alq_3 .

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